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Synthesis and Photoluminescence of $CaAlBO_4$:RE^{3+}(RE=Dy & Eu) Phosphor

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Abstract: ***A series of doped $CaAlBO_4$:RE^{3+} (RE = Dy and Eu) compositions were synthesized by wet chemical method and their photoluminescent (PL) properties were systematically investigated to ascertain their suitability for application in light emitting phosphor in lamp industry. The X-ray diffraction (XRD) pattern and surface morphology data indicates that Dy^{3+} and Eu^{3+} ions are successfully occupied non centrosymmetic site in orthorhombic crystalline phase of $CaAlBO_4$. The microstructures of $CaAlBO_4$ are studied by scanning electron microscope (SEM). The PL emission spectra of $CaAlBO_4$: Eu suggests the presence of both Eu^{3+} as well as Eu^{2+} ions. The PL emission spectra of Eu^{3+} ion was observed at 592 nm and 614 nm in red region while Eu^{2+} was observed at 430 nm in blue region in $CaAlBO_4$:Eu under 393 nm excitation. Emission at 592 nm and 614 nm are assigned to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} ion and around 430 nm assigned to $4f^65d^1 \rightarrow 8S_{7/2}4f^7$ transition in the blue region in the same phosphor. Moreover, PL emission spectra of $CaAlBO_4$: Dy was observed at 577 nm in yellow region and at 483 nm in blue region on the excitation of 351 nm. It is well known that the blue (484 nm) emission band corresponding to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ magnetic dipole transition and the yellow (577 nm) emission corresponding to the $^4F_{9/2} \rightarrow ^6H_{13/2}$ electric dipole transition. At the higher dopant concentration emission intensity quenched due to the decreased critical distance ($R_C \approx 35.81$ Å) between Dy^{3+} ions similarly critical distance between Eu^{3+} ions was $Rc \approx 48.60$ Å for maximum dopant concentration 0.2 mol.%).***

Keywords: $CaAlBO_4$; Wet chemical method; Concentration quenching; XRD; SEM and PL.

1. Introduction

Borate compounds are well known remarkably for their use in industries and mineralogy. Metal borates have excellent mechanical properties, good chemical inertness and high stability under high temperature, light weight, and low thermal expansion coefficients. Calcium borate is a potential material for applications in ultraviolet (UV) light sources, light emission diodes (LEDs), and luminescent phosphors, ceramic coatings, glass fibres and dielectric devices. Calcium borate glasses are potential candidates for optical applications due to their ease of shaping as large bulk samples or fibers [1] .Since their discovery, the uses of lanthanides in phosphors have found numerous applications in, for example, Scintillators, luminescence immunoassay and X-ray detector systems. One of the earliest applications was their use in phosphors for domestic lamps. The lanthanides possess unique properties which are responsible for their wide range of applications.

Eu^{2+}-doped phosphors usually show intense broad-band emission from deep blue to red region of electromagnetic spectrum.The emission occurs due to electronic transition between 4f7 ground state and $^4f_6 \rightarrow ^5d_1$ excited state [2,3] .Since the 5d orbital is exposed to the surrounding ions the radiative transitionis highly influenced by the crystal field components.Consequently, the wavelength of maximum emission strongly depends on the type of the host crystal [2,4].

The authors noted very sluggish crystallization behavior for the most B_2O_3 rich mixtures, and subsequent wetting and autoclave treatment at 600°C became necessary to obtain crystalline products.Two ternary phases were detected, CaAlBO4 and $CaAl_2B_2O_7$.The structure of $CaAlBO_4$ (*Ccc*2, ρ = 2.60 g/cm^3, *a* = 8.269Å, *b* = 15.227Å, *c* = 5.733 Å) is characterized by low coordination numbers for all cations: Ca is six-coordinate, Al shows tetrahedral coordination and boron is three-coordinated by O [5].Two modifications were assumed for $CaAl_2B_2O_7$: α-$CaAl_2B_2O_7$ (below 830 °C, *R*_3*c*, ρ =2.44 g/cm3, *a* = 4.810Å, *c* = 46.633 Å) with a structure of ABC-stacked modules of CaO_6 octahedra, AlO_4 tetrahedraand trigonal BO_3 groups [6]);β-$CaAl_2B_2O_7$ is assumed to be monoclinic [7].

Here we concentrate on the preparation of $CaAlBO_4$:RE^{3+} by wet chemical method. PL emission spectra of $CaAlBO_4$: Eu phosphor under UV excitation shows prominent Eu^{3+} emission peak due to $^5D_0 \rightarrow ^7F_2$ transition in the orange/ red region of the visible spectrum while Eu^{2+} emission peak due to $4f^65d^1 \rightarrow 8S_{7/2}4f^7$ transition in the blue region in the same phosphor . Moreover, PL emission spectra of $CaAlBO_4$: Dy was observed at 577 nm in yellow region and at 483 nm in blue region on the excitation of 351 nm. It is well known that the blue (484 nm) emission band corresponding to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ magnetic dipole transition and the yellow (577 nm) emission corresponding to the $^4F_{9/2} \rightarrow ^6H_{13/2}$ electric dipole transition.

2. Experimental

$CaAlBO_4$ phosphor was prepared by wet chemical method. In this process, Calcium nitrate $Ca(NO_3)_2$(99.9%), Aluminum nitrate $Al(NO_3)_3$(99.9%), Boric acid H_3BO_3(99.9%) and Ammonium nitrate NH_4NO_3used as oxidizer (All of A.R.Grade) were taken as raw materials in exact stoichiometric proportion. In addition this, rare earth elements as Dy_2O_3 (99.9%) and Eu_2O_3 (99.9%) were also taken with molar concentration as dopant respectively.

All the chemicals were dissolved separately in 50ml double distilled de-ionized water to get clear transparent solutions.

Mixture of all the solutions which is nothing but theCaAlBO4: Ln solutions were then heated to 80ºC for 8 hrs on magnetic stirrer. The dried sample was then crushed using mortar pestle and quenched at 200ºC for 2 hrs so as to obtain a luminescent $CaAlBO_4$ borate phosphor. This phosphor was then taken for characterization. The crystallographic phase identification of synthesized powder samples was carried out by X-ray diffraction (XRD, PHILIPS P Analytical XPERT-PRO Diffractrometer) using Cu-Kα wavelength (λ=1.54060 Å) and scanning in 2θ range from 10° to 80^o. The emission and excitation spectra were measured on a SHIMADZU RF-5301 PC fluorescence spectrophotometer. The surface morphology of $CaAlBO_4$: RE^{3+} (RE: Dy and Eu) was performed by a scanning electron microscope (SEM: JEOL-JSM-6360LV).

3. Results and Discussion

3.1 Crystal structure and surface morphology of $CaAlBO_4$

The XRD pattern of the $CaAlBO_4$ presented in fig.1,which is in good agreement with the XRD data of standered $CaAlBO_4$ with JCPDS card (19-0204). This compound crystallizes in an orthorhombic unit cell of a = 8.27Å, b =15.23 Å and c= 5.73 Å. The microstructures of $CaAlBO_4$ are studied by scanning electron microscope (SEM). The sample synthesized through wet chemical route; platelet like structures with other fluffy shapes is obtained with non-uniform distribution.

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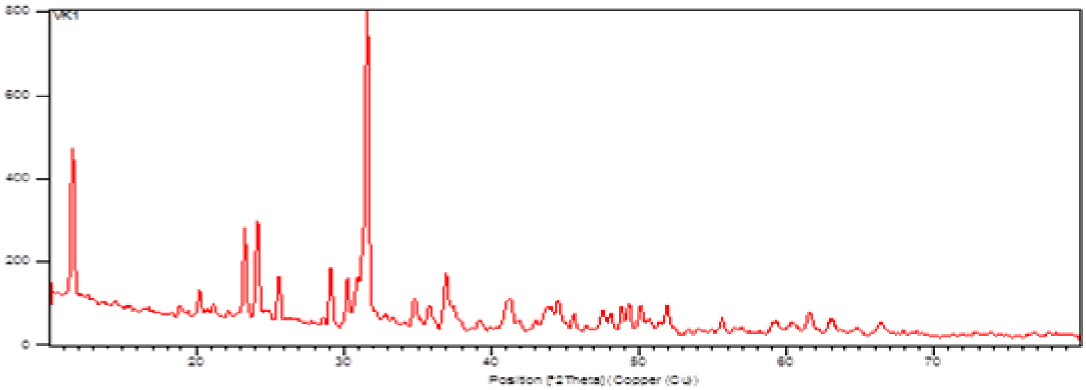

Figure 1: X-ray diffraction pattern of $CaAlBO_4$ host

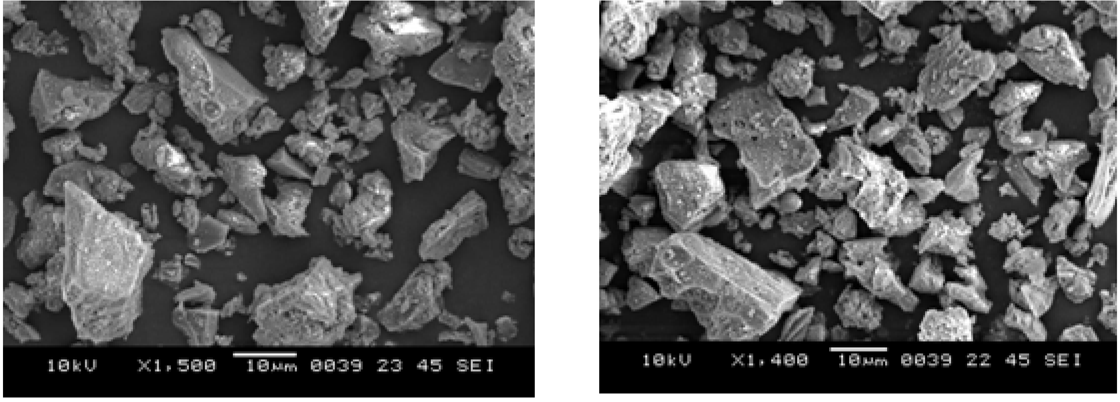

Figure 2: Surface morphology of $CaAlBO_4$ host

3.2 PL characteristics of $CaAlBO_4$:Dy^{3+}

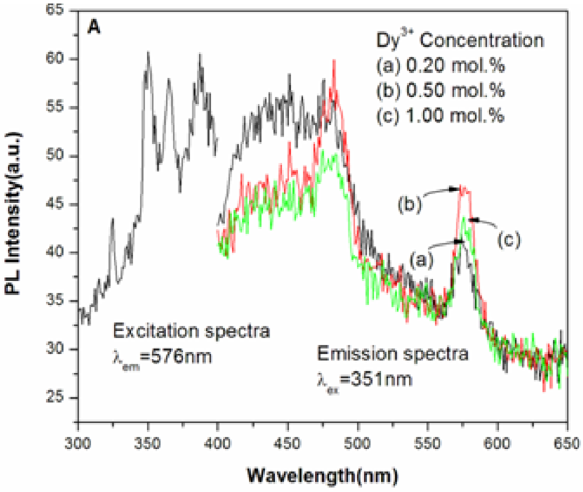

Figure 3(A): PL emission spectra of $CaAlBO_4$ under excitation of λ_{ex}=351nm.

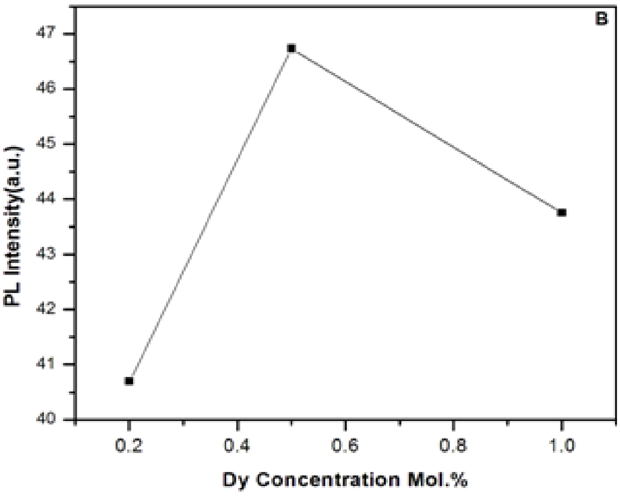

Figure 3(B). The variation of PL intensity with Dy^{3+}concentration

The emission spectra of $CaAlBO_4:Dy^{3+}$ phosphors recorded excited at UV (351 nm) light as shown in fig.3.(A) Excitation spectrum also shown in fig.3,(A), the prominent narrow absorbance band centered at 351 nm recorded at the emission 576 nm. There are two peaks observed from the emission spectra of the phosphor. The first two prominent peaks centered around 484 nm and other 576 nm. These emission peaks in the blue, and yellow region are the characteristics emission of the Dy^{3+} ions and frequently seen in Dy^{3+} doped phosphors [8-11].

The peaks position and the Y/B (yellow/blue) intensity ratio altered due to the influence crystal field effect of the host materials on the emission of Dy^{3+} ions. It is well known that the blue (484 nm) emission band corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ magnetic dipole transition less influenced by crystal field effect compare to the yellow (577 nm) corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric dipole transition, its $\Delta J=2$ ultra-sensitive transition[12].It is well known that the blue emission is of magnetic dipole origin and the yellow one is predominant only when Dy^{3+} are located at low-symmetry siteswith no inversion centers [13]. Since emission intensity of the blue emission is stronger than that of the yellow one in the investigated phosphors, which suggests that there is very little deviation from inversion symmetry in the investigated phosphors.

In our case the Dy^{3+} ion may enter the host lattice to substitute $Ca^{2+,}$ or Al^{3+}or it may be located on surfaces of the crystals due to the porous structure. It is clear from the photo- luminescence spectra that in the Dy^{3+} doped phosphor, energy transfer from the host to the Dy^{3+} activator ions occurs.The ionic radii of Dy ions is 91.2 pm,which is similar to those of the Ca^{2+} ions (99pm) .In our case the Dy^{3+} ion may enter the host lattice to substitute Ca^{2+} or locate on surfaces of the crystals lattice.It's substitution at Ca^{2+} site in $CaAlBO_4$ will lead to less distortion and induce more oxygen vacancies in the host phosphor. The charge compensating effects in the immediate vicinity is likely to influence the local site symmetry of $CaAlBO_4$ host. Dy^{3+} ions should occupy statistically both cation positions (Ca^{2+}) in the unit cell..It would naturally cause a substantial number of vacant sites in the oxygen ion array and then expand the lattice to decrease crystal density[14], reported that the oxygen vacancies might act as the sensitizer for the energy transfer to the rare earth ion due to the strong mixing of charge transfer states result in the highly enhanced luminescence. But excess oxygen vacancies in the host would destroy the crystallanity inevitably,which leads to quenching of the luminescence [15]. As Dy^{3+} ions progressively replace the Ca^{2+} ions, it can enhance PL emission intensity and progressively reduce asymmetry factor. The low-symmetry location of Dy^{3+} results in predominant emissionof $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition in $CaAlBO_4$ host.

In principle, if there is an increase in concentration of the lanthanide ions in a given material it should be accompanied by an increase in the emitted light intensity, but it has been established that such behavior occurs up to a certain critical concentration [16].Above this critical concentration the luminescence intensity starts to decrease. This process is known as concentration quenching of the luminescence. Concentration quenching occurs as a result of a very efficient energy transfer process between the luminescent centers; it starts to have significant effect at a concentration for which there is a considerable reduction in the mean distance between the interacting centers. Two mechanisms are generally invoked to explain the concentration quenching: energy transfer between the lanthanide ions and defects of the host, and interactions between the lanthanide ions.

In the first case due to a very efficient energy transfer, excitation energy migrates to a large number of centers being finally transferred to lattice defects or impurity ions that act as energy acceptors. These acceptors can relax to their ground state by multi-phonon emission or light emission at wavelengths different from those characteristic of the lanthanides. These kinds of energy acceptor centers are called *killer* or *quenching traps*, and acts as energy sink within the chain transfer, thus quenching the luminescence of the lanthanide ions. The second type of mechanisms is due to energy dissipation via cross relaxation by means of resonant energy transfer between two identical adjacent centers. At large concentrations new kind of centers can be formed, due to clustering of the individual ions. This leads to rearrangements of the energy levels that can strongly affect the fluorescence properties [17].

Fig. 3(A). shows the PL spectra of $CaAlBO_4:xDy^{3+}$ phosphors excited by 351 nm light. The PL intensity of both blue and yellow emissions increases with the growing content of Dy^{3+} ions until reaching a maximum at x = 0.50 mol.% and then it decreases because of concentration quenching, as shown in Fig 3(B).

Obviously, the optimal dopant concentration of Dy^{3+} is 0.5 mol. %, which means the PL intensity of emission peaks decrease while the doped content is above 0.5 mol. % because of the quenching concentration of Dy^{3+}.The critical distance Rc of the energy transfer between the same activators Dy^{3+} in $CaAlBO_4$ phosphor could be estimated according to the following equation [18,19].

$$R_c \approx 2\left(\frac{3V}{4\pi X_c Z}\right)^{1/3} \quad (1)$$

Where Xc is the critical concentration, Z is the number of Ca^{2+} ions in the unit cell and V is the volume of the unit cell.By taking experimental value and analytical values of Xc, Z and V (0.005, 6 and 721.705 Å^3).The critical transfer distanceof Dy^{3+} in $CaAlBO_4:xDy^{3+}$ phosphor was estimated to be about 35.81Å.

3.3 PL characteristics of $CaAlBO_4:Eu^{3+}$

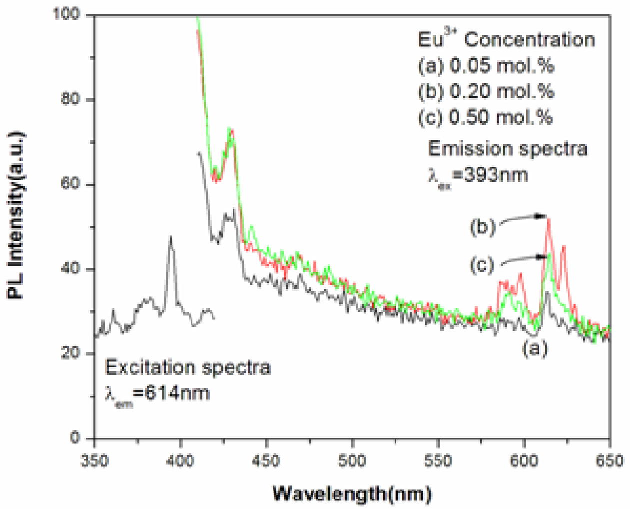

Figure 4: PL emission spectra of $CaAlBO_4$ under excitation of λ_{ex}=393nm.

The emission spectrum is composed of s series sharp peaks from 570 nm to 650 nm which are attributed to the transition $^5D_0 \rightarrow {}^7F_J$ (J=0-3). It is accepted that the selection rule of electric dipole (ED) transition is $\Delta J \leq 4$, when J or J'=0, $\Delta J=2$ and selection rule for magnetic dipole (MD) transition is $\Delta J=0, \pm 1$.Thus, the highly intense line $^5D_0 \rightarrow {}^7F_1$ is because of magnetic dipole transition. The main emission bands centered at 614 nm is attributed to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ which is ascribed to the lifting of the spin and parity prohibitions of $Eu^{3+} f - f$ transitions in $CaAlBO_4$ host lattice. Because of the crystal field effect, ^7F_J energy level will appear Stark levels. Therefore, the energy level transition $^5D_0 \rightarrow {}^7F_1$ is split into 589 nm and 598 nm emission peaks and $^5D_0 \rightarrow {}^7F_2$ is split into 612 nm and 623 nm. This transition is coming from the relaxation of selection rule somewhat because the crystal field plays a role in mixing states.

Fig. 4 shows, PL emission spectra of Eu^{3+} ion in $CaAlBO_4$: xEu with different concentration under excitation of 393 nm. Two resolved peaks are observed around 592 nm and 614 nm, which are assigned due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition Eu^{3+} ion and around 430 nm assigned due to $4f^6 5d^1 \rightarrow 8S_{7/2} 4f^7$ transition in the blue region in the same phosphor. The $^5D_0 \rightarrow {}^7F_2$ transition is corresponds to electric dipole transition while $^5D_0 \rightarrow {}^7F_1$ transition is corresponds to magnetic dipole transition.

In this host, it is also found that for less than 0.20 mol. % concentrations PL intensity is weak. Hence material is suitable for 0.20 mol. % concentrations. The intensity peaks 614 nm are more intense than the peaks at 430 nm with increasing concentration of Eu in $CaAlBO_4$, which indicates that the red region intensity is more than blue region intensity. Hence this material is suitable for 0.20 mol. % concentrations in red region while it is suitable for 0.50 mol. % in blue region. The trivalent europium ion is very useful for studying the nature metal coordination in various systems, owning to its non-degenerate emitting $^5D_0$ state and for lamp phosphor.

Normally, with different amounts of Eu^{3+} doped into the host lattice, the local surroundings around a substituted site will be changed, which eventually makes it possible to tune the luminescence properties. By investigating the emission intensity of $CaAlBO_4$ doped with different Eu^{3+} contents excited at 393 nm, we get the dependence of the corresponding PL intensity as a function of Eu^{3+} concentration. Obviously, the optimal dopant concentration of Eu^{3+} is 0.20 mol. %, which means the PL intensity of emission peaks decrease while the doped content is above 0.20 mol. % because of the quenching concentration of Eu^{3+}.

According to equation 1, the critical distance between Eu^{3+} ions of $CaAlBO_4{:}xEu^{3+}$ phosphor was estimated to be 48.60Å, by taking experimental value and analytical values of Xc, Z and V (0.002, 6 and 721.705 $Å^3$).

4. Conclusions

Rare earth doped $CaAlBO_4$: Dy and $CaAlBO_4$:Eu phosphors by wet chemical method. Blue emission is typical emission of Dy^{3+} corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and yellow emission corresponding to $^4F_{9/2} \rightarrow {}^6H_{13/\ 2}$ transition. The entire characteristic indicates that $CaAlBO_4$: Dy phosphor is good candidate for solid state lighting device application.

The PL emission spectra of $CaAlBO_4$: Eu phosphors suggest that presence of both Eu^{3+} ion as well as Eu^{2+} in $CaAlBO_4$ lattice sites.PL revealed that Eu^{3+} gives broad band emission of orange/red region due to $^5D_0 \rightarrow {}^7F_2$ transition while Eu^{2+} emission peak due to $4f^6 5d^1 \rightarrow 8S_{7/2} 4f^7$ transition in the blue region in the same phosphor. The trivalent europium ion is very useful for studying the nature of metal coordination in various systems, owning to its non-degenerate emitting $^5D_0$ state and for lamp phosphor.

5. Acknowledgements

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